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Weathering of volcanic rocks from Mt. Vesuvius associated with the lichen *Stereocaulon vesuvianum*

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With 10 figures

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1. Introduction

The effectiveness of lichens as agents for rock weathering and soil formation has long been recognized (FRY, 1927; JACKSON & KELLER, 1970; ASCASO *et al.*, 1976; JONES *et al.*, 1980; GALVAN *et al.*, 1981; JONES *et al.*, 1981; WILSON *et al.*, 1981; WILSON & JONES, 1984; JONES & WILSON, 1985). Lichens are among the first organisms to colonize a freshly exposed rock surface. Such lichen-encrusted rocks provide an ideal environment for studying the biogeochemical weathering of minerals since, unlike the situation in soil, the influence of only two organisms — the alga and the fungus — on any one mineral, have to be investigated. SYERS & ISKANDAR (1973) suggest that it is convenient to evaluate the pedogenetic significance of lichens in terms of the biogeophysical and biogeochemical processes involved in the weathering of rocks. The most important mechanisms implicated in the physical weathering of the substratum are:

- rhizine penetration;
- thallus expansion and contraction.

The main chemical processes by which lichens are able to decompose minerals are:

- the production of CO₂;
- the excretion of oxalic acid;
- the production of water-soluble biochemical compounds called lichen acids.

In the present paper the changes induced by the growth of the fruticose lichen *Stereocaulon vesuvianum* on leucitic rocks of Mt. Vesuvius have been studied.

2. Materials and methods

Stereocaulon vesuvianum (PERS.) is widespread on leucite-bearing rocks of Mt. Vesuvius, 12 km south-east of Naples in the Campania Region.

Samples of lichen, lichenized volcanic rock and substrate at the interface between the rock and the lichen thallus were collected. Optical and S.E.M. observations were made upon:

- fragments of lichen-encrusted rock;
- mineral grains remaining after hydrogen peroxide treatment of scraped weathered material beneath the lichen;
- the rock surface immediately below the lichen.

For scanning electron microscopy the samples were mounted with colloidal carbon on aluminium stubs, were coated with carbon or with gold and were examined in a Cambridge Stereoscan 250 Mk2 instrument equipped with an energy dispersive X-ray analyser. In order to study closely the nature and composition of the weathered material at the interface between the rock and the lichen thallus, the silt, clay and fine clay ($\varnothing < 0.5 \mu\text{m}$) fractions were separated, after H₂O₂ treatment, from the scraped substrate beneath the lichen.

These fractions were examined by X-ray diffraction, transmission electron microscopy and I.R. spectroscopy.

A Philips 2kW X-ray diffractometer with iron filtered $\text{CoK}\alpha$ radiation was used to record X-ray powder patterns. For the T.E.M. observations a Siemens Elmiskope 102 instrument was used.

Infrared spectra were recorded with a Perkin Elmer 567 Spectrometer using 13 mm-diameter KBr pressed disks containing 0.8 mg of sample.

Dry deposition collected by washing the fresh thallus samples was analyzed for organic and inorganic anions by ion chromatography using a Dionex SP/2000i instrument (analytical column AS4A; guard column AG4A; fiber suppressor). The eluent used was $0.75 \times 10^{-3} \text{ M NaHCO}_3$ in $2.2 \times 10^{-3} \text{ M Na}_2\text{CO}_3$ at a flow rate of $2 \text{ cm}^3 \text{ min}^{-1}$ with a pump pressure of 7000 kPa.

3. Results

3.1. Optical observations

The substrate rock is a vesuvite. The dominant minerals are leucite, occurring as large pseudo-isometric crystals and exhibiting extremely weak birefringence with low first-order grey interference colours and low relief, and augite, readily identified by its optical properties. Both leucite and augite crystals are surrounded by the dark-grey, homogeneous, microcrystalline matrix, which consists largely of calcium-rich plagioclase feldspar.

The interface between the rock and the lichen is not well defined and there is clear evidence of disruption of the rock surface. The "roots" of the lichen had penetrated deeply into the rock.

3.2. S.E.M. observations

The rock-lichen interface is characterized by extensive disintegration of the rock surface with separation of numerous rock fragments (figure 1a).

Many of them are located immediately beneath the lichen thallus, and others are incorporated into the thallus (figure 1b). The X-ray spectra from all of these mineral fragments are dominated by aluminium, silicon, potassium and calcium but appreciable amounts of iron, magnesium and sodium can also be detected (figure 2 a, b, c). These results indicate that the mineral fragments are fragments of vesuvite substrate. Nevertheless some

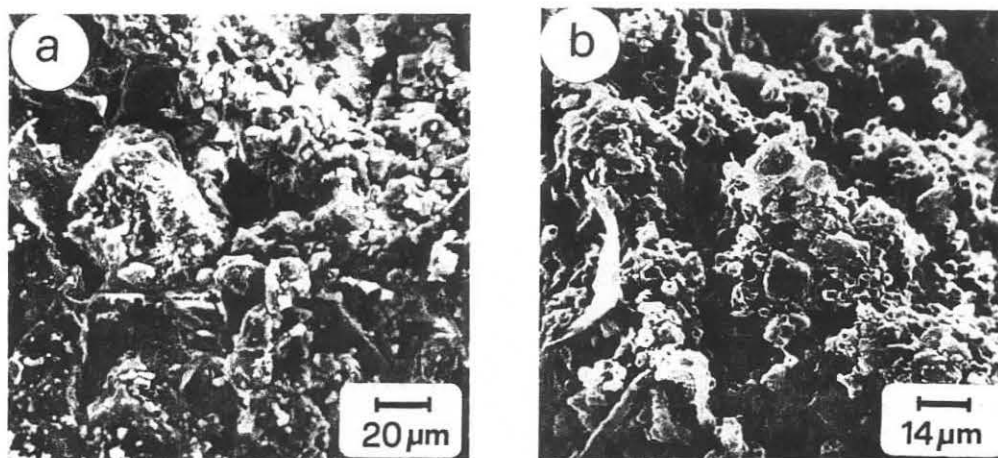


Fig. 1. Scanning electron micrographs (SEM) of volcanic rock-*Stereocaulon vesuvianum* lichen interface showing extensive disintegration of the rock surface (a); volcanic rock fragments in lichen thallus (b).

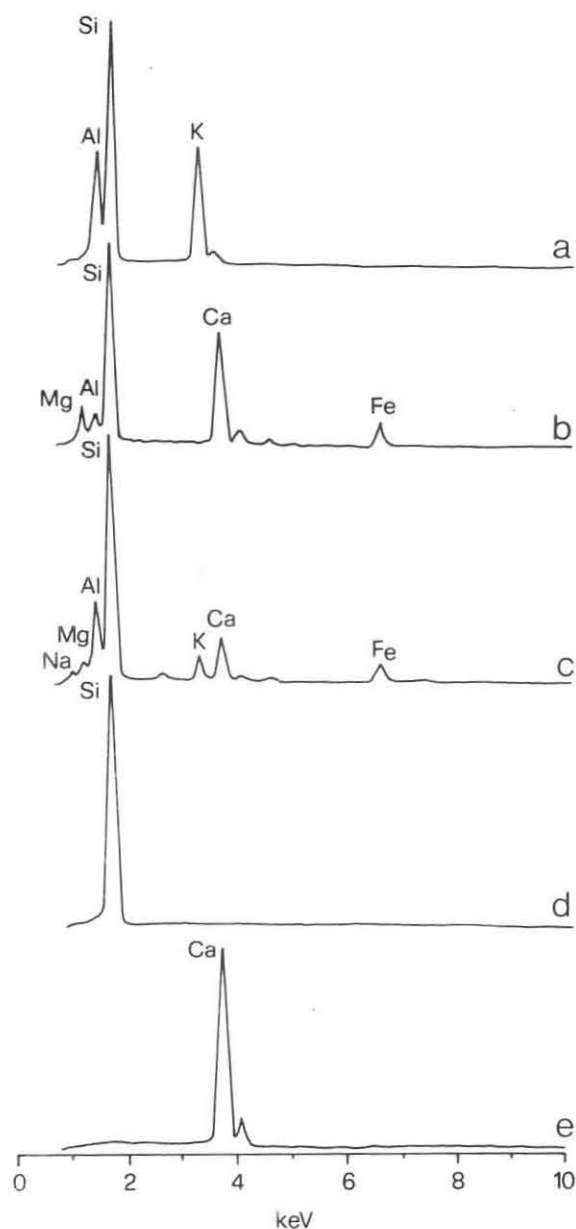


Fig. 2. X-ray spectra of mineral fragments directly beneath lichen and in the lichen thallus. Leucite (a); augite (b); plagioclase feldspar (c); quartz (d); calcium oxalate (?) (e).

fragments observed in the lichen thallus yielded X-ray spectra completely dominated by silicon (figure 2d) and calcium (figure 2e).

The surfaces of mineral grains found at the rock-lichen interface or embedded in the thallus are extensively etched. Electron probe microanalysis enabled differentiation of the separate minerals, these being mainly leucite and augite. Leucite is characterized by rounded etch pits (figure 3a), and augite by two sets of cleavage planes at right angle to each other (figure 3b).

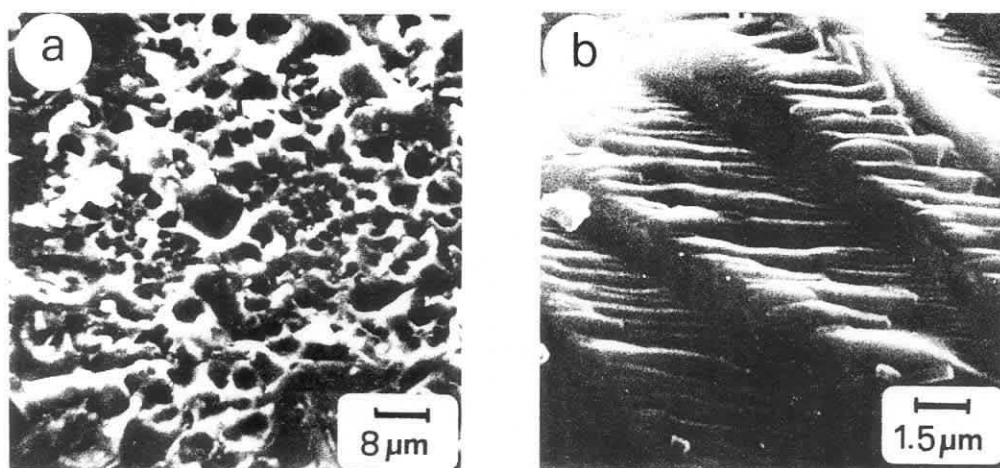


Fig. 3. Scanning electron micrographs (SEM) of weathered mineral grains at the rock-lichen interface and in the thallus of *Stereocaulon vesuvianum*. Rounded etch pits in leucite (a); etched cleavage planes of augite (b).

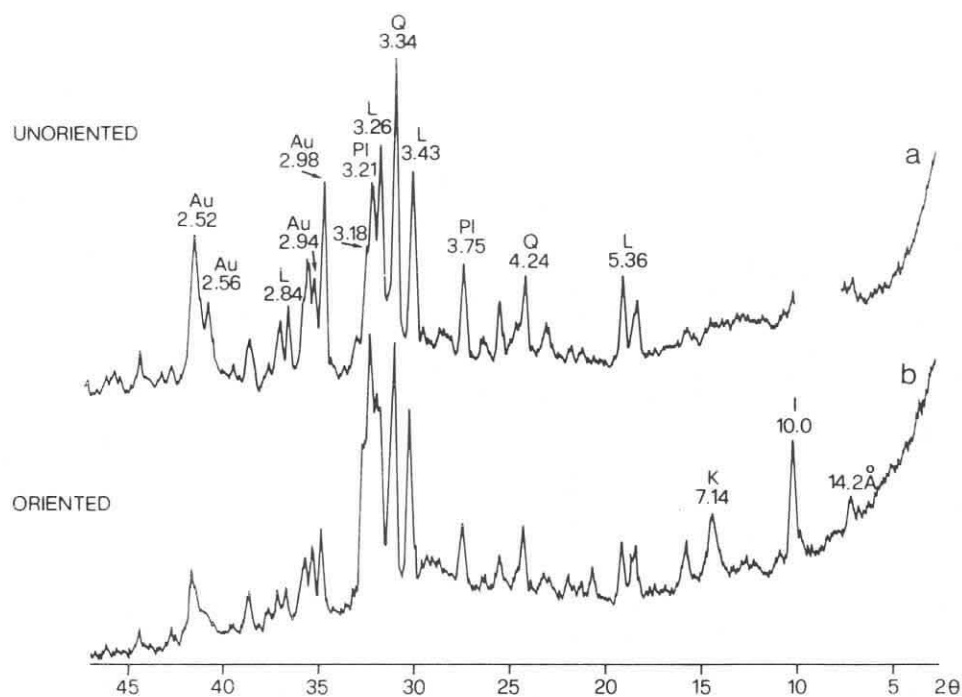


Fig. 4. X-ray diffractometer traces (CoK α radiation) of the silt fraction from the weathered material beneath the lichen. Unoriented (a) and oriented mount (b). L = leucite, Au = augite, PI = plagioclase feldspar, Q = quartz, K = kaolinite, I = illite.

3.3. X-ray diffraction

The unoriented and oriented mounts of the silt fraction from the weathered material beneath the lichen yielded X-ray diffractometer traces which could be interpreted in terms of a mixture of rock-forming minerals, according with the E.D.X.R.A. results presented above (figure 4a, b).

The reflections which occur at 5.36, 3.43 and 3.26 Å [$1 \text{ Å} \triangleq 1 \cdot 10^{-10} \text{ m} = 10 \text{ nm}$] correspond to the main diagnostic reflections of leucite, at 2.98, 2.94 and 2.52 Å to augite X-ray reflections, at 3.75, 3.21 and 3.18 Å to plagioclase feldspar lines.

A small amount of quartz also occurs, as indicated by the diagnostic peaks at 4.24 and 3.34 Å. The presence of this mineral in the thallus clearly indicates that contamination from aeolian sources had occurred, as quartz does not occur in the substrate rock.

The oriented mounts prepared by sedimenting the silt fraction on glass slides reveal also the presence of various clay minerals (figure 4b).

X-ray diffraction traces of the clay fraction of the weathered material beneath the lichen confirm the clay minerals presence (figure 5a). Ethylene glycol solvation and heating at 550 °C demonstrate kaolinite and illite presence (figure 5b–c). A rather high background at about 3.5–4.5 Å suggests the presence of amorphous material. This is consistent with X-ray diffraction observations on the fine clay fraction ($\varnothing < 0.5 \mu\text{m}$) which indicate the presence of appreciable amounts of amorphous material.

The reflections at 6.20 and 4.45 Å in the X-ray diffractometer traces of the clay fraction and the reflections at 5.95 and 2.97 Å in the X-ray diffractometer trace of the powdered thallus (figure 6) suggest the presence of the monohydrate and dihydrate forms of calcium oxalate.

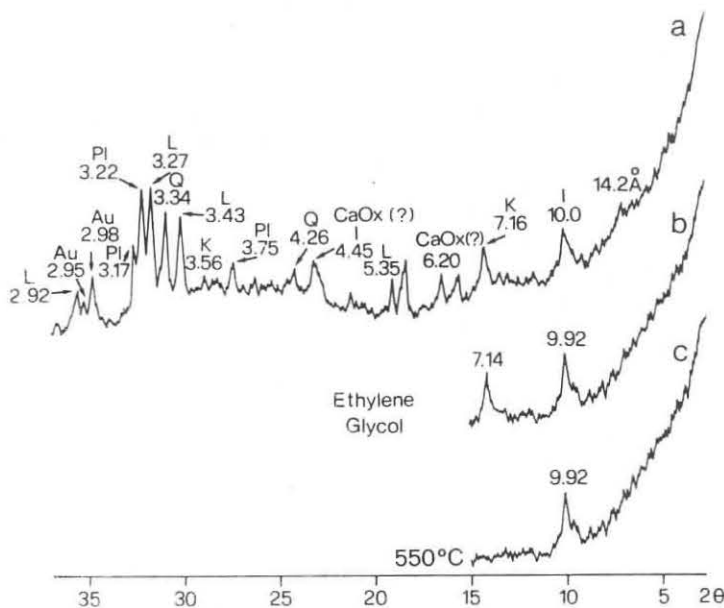


Fig. 5. X-ray diffractometer traces (CoK α radiation) of the clay fraction from the weathered material beneath the lichen. Oriented mount (a), ethylene glycol solvated (b) and heated at 550 °C (c). L = leucite, Au = augite, Pl = plagioclase feldspar, Q = quartz, K = kaolinite, I = illite, CaOx = calcium oxalate.

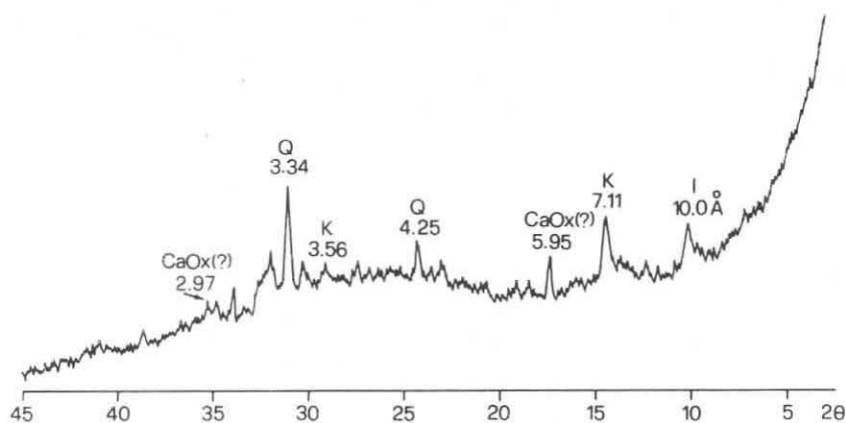


Fig. 6. X-ray diffractometer trace ($\text{CoK}\alpha$ radiation) of powdered lichen thallus. K = kaolinite, I = illite, Q = quartz, CaOx = calcium oxalate.

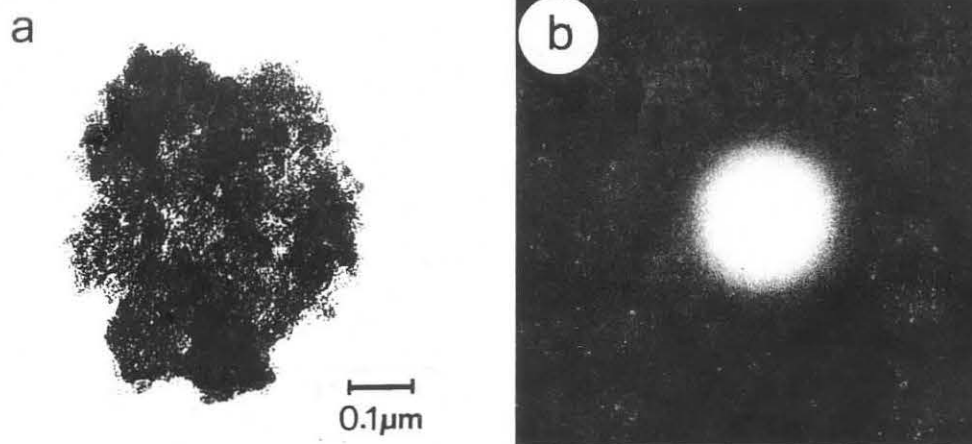


Fig. 7. Transmission electron micrograph (TEM) of fine clay fraction ($\varnothing < 0.5 \mu\text{m}$) (a); electron diffraction pattern from selected area of microaggregates (b).

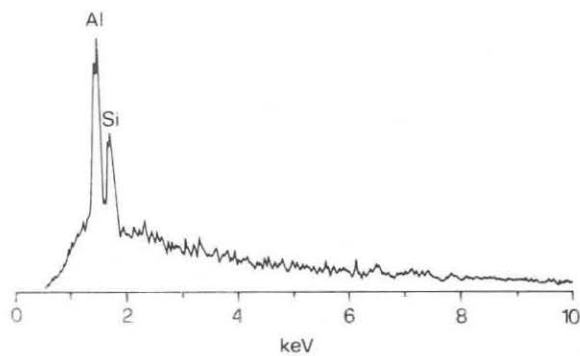


Fig. 8. X-ray spectrum of fine clay fraction ($\varnothing < 0.5 \mu\text{m}$).

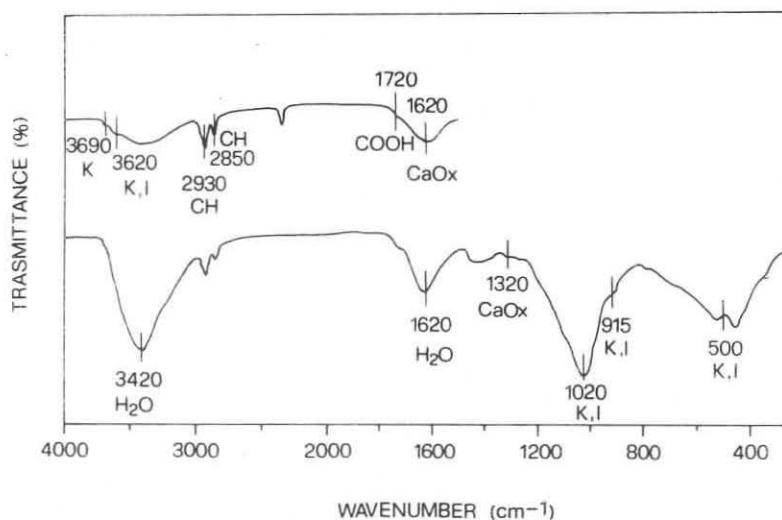


Fig. 9. Infrared spectra of fine clay fraction ($\phi < 0.5 \mu\text{m}$).

3.4. T.E.M. observations

Transmission electron microscopy reveals that the fine clay fraction ($\phi < 0.5 \mu\text{m}$) consists of microaggregates of very finegrained particles (figure 7a). These microaggregates give a weak electron diffraction pattern with diffuse and poorly defined rings (figure 7b) consistent with amorphous material and in agreement with X-ray diffraction results.

Microanalysis of these microaggregates showed that they contain considerable amount of aluminium and silicon (figure 8) suggesting the presence of amorphous aluminosilicates.

3.5. Infrared spectroscopy

Infrared spectroscopy confirms the presence of kaolinite and illite. The rather wide band at 3500 cm^{-1} is assignable to the presence of poorly-ordered material (figure 9). Additional bands at 2930, 2850, 1750, 1620 and 1320 cm^{-1} can be attributed to organo-mineral complexes and to small amounts of calcium oxalate. It is concluded, therefore, that the finegrained material from the rock-lichen interface consists of a mixture of rock-forming minerals, of clay minerals and of poorly ordered aluminosilicate.

3.6. Ion chromatography

The concentration of oxalate detected in the dry deposition ranged between 4.64 and 7.50 ppm (figure 10).

4. Discussion and conclusions

All the results presented provide information on the physical and chemical processes of weathering associated with the growth of *Stereocaulon vesuvianum* on leucitic Mt. Vesuvius rocks. The optical observation on the interface between the rock and the lichen clearly

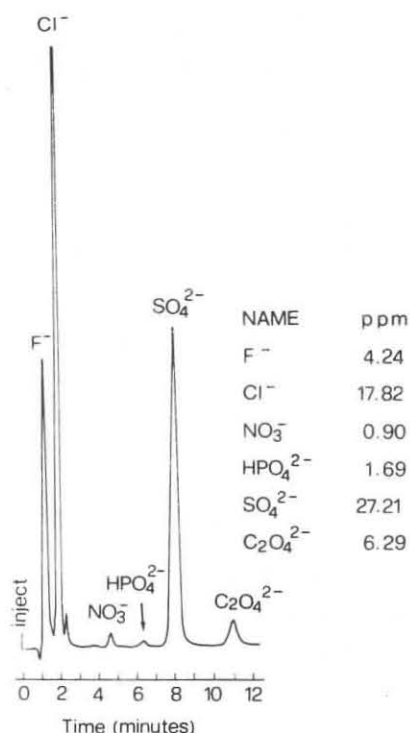


Fig. 10. Dry deposition: typical chromatogram.

shows a very deep physical disaggregation of the substrate rock by the lichen covering. Such intense disaggregation is a result of both the physico-chemical properties of the substrate rock and the nature of the lichen thallus. The mineralogical composition of lavic rock and the presence in it of many vesicles and less coherent areas make the penetration of the pseudopodetio and its ramifications easier.

The typically strong adhesion of *Stereocaulon vesuvianum* to the substrate added to the thallus expansion and contraction, promote disaggregation of the rock surface, the detachment of mineral fragments and their incorporation into the thallus. The chemical – or biogeochemical – decomposition of rock substrate proceeds at the same time as the physical – or biogeophysical – disintegration, as shown by the extensive surface etching in the grains incorporated into the lichen thallus and in the rock surfaces immediately below the lichen. The only secondary products which seem to have formed as a result of such chemical weathering are poorly ordered alumino-silicate materials and various clay minerals. These products occur intimately admixed at the rock-lichen interface.

In these circumstances most, if not all, of above changes could be accounted for the reactions of lichen acids with the mineral particles. The present study does not provide enough evidence to consider calcium oxalate a product of lichen weathering of rockforming minerals. Calcium oxalate crystals were not observed by Scanning Electron Microscopy (SEM) and, furthermore, the treatment of weathered material beneath the lichen with hydrogen peroxide could produce oxalates. Nevertheless it is not possible to exclude completely the effects of oxalic acid as well as of other low-molecular-mass organic acids produced by the mycobiont.

5. References

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The weathering phenomena resulting from the colonization of leucitic rocks of Mt. Vesuvius by *Stereocaulon vesuvianum* (PERS.) lichen have been studied. Lichen weathering results in the disruption of the rock substrate and in the extensive etching and degradation of the primary rock-forming minerals particularly leucite and augite to yield poorly ordered aluminosilicate materials and clay minerals. It is suggested that the weathering process could be accounted for the reactions of lichen acids with the mineral particles. Nevertheless it is not possible to exclude completely the effects of oxalic acid as well as of other low-molecular-mass organic acids produced by the mycobiont.

Key words: weathering, leucitic rock, lichen, lichen acids, oxalic acid, mycobiont.

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